

The University of Chicago

THE EFFECT OF A STRONG MAG-
NETIC FIELD ON THE ELECTRODE
POTENTIALS OF IRON AND NICKEL

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1931

By
ETHEL EVERETT LIND

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The influence of a magnetic field on the potentials of metals has been the subject of a number of experimental investigations. For the most part, researches indicate that magnetization does have an effect on the potentials of the ferromagnetic metals, iron and nickel, but investigators disagree as to the cause and nature of the effect. Even experimental results seem to differ.

Remsen,¹ in 1881, found that when ferrotype iron, such as is used in tintype photography, was bent in the form of a small tray to contain a solution of copper sulfate and set on the poles of a magnet, the replacement of copper from solution formed a design similar to that produced when iron filings are sprinkled on a piece of paper laid on the poles. He further noted the protection of the iron from chemical action in lines around the edges of the poles.

Gross² investigated the current produced in a cell consisting of two similar iron electrodes so placed in a cell that one was influenced by a magnetic field and the other was not. No definite current was observed if concentrated solutions of ferrous salts were used as electrolytes, but if sol-

¹Remsen, Am. Chem. Journal, 3, 157 (1881).

²Gross, Sitz. Ber. d. Kais. Akd. Wiss, 92, 1373 (1885).

utions of ferric salts were used the current flowed first in one direction and then reversed to become constant in the second direction. The final current flowed within the solution from the magnetized to the unmagnetized electrode, that is, the electrode within the field was the negative terminal of the cell. The naive conclusion which Gross drew from his experiment was that the highest electrode potential would exist at that electrode on which the maximum work was performed.

Experiments of a similar nature were carried out by Andrews,¹ in which he used as electrolytes strong oxidizing agents and acids. In those solutions in which ferric salts were formed the same current direction as Gross obtained was observed, but in hydrochloric and sulfuric acids the current direction was reversed. Andrews' conclusion was that the magnetized electrode was more rapidly acted upon than the unmagnetized one.

Rowland and Bell² used for electrodes two bits of iron wire about one millimeter in diameter and ten millimeters long imbedded in insulating material and arranged so that the wires were in the direction of the lines of force. One wire was filed to a point and the other exposed on a portion of the side. The electrolytes used were a ferric salt and acids. When both electrodes and the surrounding solution

¹ Andrews, Proc. Roy. Soc., 42, 459 (1887); 44, 152 (1888).

² Rowland and Bell, Am. Journ. of Science, 36, 39 (1888).

were put into the magnetic field, a current flowed in the same direction as if the sharp-pointed pole had been replaced by copper and the other by zinc, that is, the sharp-pointed pole was positive and the other negative. The deflection of the galvanometer needle was not permanent, but the needle returned slowly toward its starting point and indeed was deflected in the opposite direction. Rowland and Bell considered the first effect the primary one due to the magnetic field and the reversal of current a secondary effect due to other factors. It was further noted that if both pieces of iron had flat surfaces or if the electrodes were held perpendicular to the lines of force, the effect of the magnetic field disappeared completely. The effect of the field amounted to a change of 0.0001 to 0.03 volts in the electromotive force of the cell. (The effect obtained with nickel was similar in nature but less in magnitude.) These investigators explained their results in the following manner: Since the force acting on a particle in any direction is proportional to the rate of variation of the potential in that direction, and the rate of variation is greatest near the edges and points of a magnetic pole, more work would be required to tear away a particle of iron from such points than from a hollow. Remsen's experiment was cited as another example of this fact.

Squier¹ held that the action of the magnet which

¹Squier, Am. Jour. of Science, 45, 443 (1893).

caused the electrode in the field to become more positive, was the primary action. The reversal of the current, he believed, was caused by the collection of iron salt around the induced pole of the electrode. When nitric and hydrochloric acids were used as electrolytes, the maximum change in E.M.F. amounted to 36 millivolts in a field of 10,000 gauss. On further strengthening of the field, this value did not change.

With a field strength of from 916 to 9320 units, Hurmucescu¹ found a change in E.M.F. of iron in oxalic and acetic acids which amounted to between 0.002 and 0.014 volts. The current direction was the same as that observed by Squier and Rowland. The magnitude and direction of the current were explained by Duhem's² theory.

Duhem's treatment of the question was purely theoretical. He attempted to derive the work equivalent of the current accompanying the magnetization on a thermodynamic basis. Using the cell Fe, FeSO_4 , CuSO_4 , Cu, he calculated the decrease of thermodynamic potential for the chemical reaction and set this proportional to the E.M.F. obtained on magnetization.

The expression obtained was:

¹Hurmucescu, Eclair Electr. Nr. 6, 7, (1895). (Original article not available. The information was obtained from the article by Bucherer¹, page 5.)

²Duhem, Wied. Ann. 13, 101 (1889).

$$E = \frac{M^2 \lambda}{2 S F}$$

where E is the change of electromotive force on magnetization, λ the electrochemical equivalent of iron, S the specific gravity of iron, M the magnetic intensity, and F the magnetization coefficient.

Bucherer¹ was unable to obtain any change in E.M.F. as great as 10^{-5} volts when he used bundles of soft iron wires as electrodes in a solution of ferrous ammonium sulfate. The field strength which he used, however, amounted only to 1200 lines per square centimeter. In other electrolytes, that is, ferric salts and solutions in which ferric salts are formed, the magnetized electrode was always the more negative. Bucherer's conclusion was that the current obtained in solutions which produce ferric salts was due to the change in the concentration of ferrous and ferric salts at the electrode. The first effect produced by the magnet in the opposite direction he attempted to show was caused by the sudden jerk of the electrode when the magnet was first turned on.

Nichols and Franklin² used soft iron wire electrodes in a number of electrolytes. In various forms of apparatus the currents due to magnetization did not always flow in the

¹Bucherer, Wied. Ann. 58, 564 (1896).

²Nichols and Franklin, Am. Jour. of Science, 31, 272 (1886).
34, 419 (1887).
35, 290 (1888).

same direction. When a cylinder of soft Norway iron, coated with wax except for a single portion of its surface, was used as an electrode in the field, the E.M.F. developed between the terminal in the field and a similar one outside was found to depend on the portion of the bar exposed. When the exposed portion was in the neighborhood of an induced pole within the cylinder, it became more negative than the electrode outside of the field. If the exposed surface was in a neutral portion of the bar, the E.M.F. was in the opposite sense. A reversal of the direction of the current could be obtained by turning the bar, exposed at one end, in the field. When the axis of the bar was parallel to the lines of force and it was accordingly magnetized longitudinally, it acted as a negative pole. When turned upon an axis perpendicular to the line joining the poles of the magnet, the bar became magnetized transversely and the direction of the current was reversed.

The E.M.F. produced on magnetization greatly increased with the field strength and reached a value of about 68 millivolts in a field of 20,000 gauss when iron and platinum electrodes were dipped in a solution of potassium dichromate in dilute sulfuric acid.

The change of E.M.F. was attributed to a change of ferric to ferrous salt at the electrode.

Elias,¹ in reviewing the work done by the previous

¹Elias, Verslag Akad. Wetenschappen, 23, 455 (1914).

investigators, remarked that Duhem's formula, which may be expressed,

$$E = \frac{B^2 \lambda}{8 \pi d \mu} \cdot \left(1 - \frac{1}{\mu} \right)$$

where μ is the susceptibility, was μ times too small in consequence of an inaccurate expression for the energy of the magnetic field. By approximation, since μ has a large value, he wrote the equation,

$$E = \frac{B^2 \lambda}{8 \pi d}$$

and stated that it can be expected to hold only if the electrolyte is a neutral solution of a ferrous salt. Consequently only the one experiment of Bucherer's could have been expected to give values of the order of magnitude demanded by the equation. But Bucherer's field strength of 1200 gauss was not sufficient to produce an E.M.F. greater than 10^{-7} volts, whereas the method of measurement could not detect a value less than 10^{-5} volts.

Elias realized that the results of the other investigators who worked with acids, oxidizing agents, and ferric salts, could not have been expected to give values comparable with the theoretical results.

With electrodes of electrolytic iron in a 5 per cent solution of ferrous sulfate, Elias obtained, on magnetization of one electrode, changes of E.M.F. which were in accord with the theory in direction but much greater in magnitude. Be-

tween field strengths of 0 and 20,000 gauss, the changes in E.M.F. were ten to twenty times the expected values. At first, the changes were about proportional to the second power of the field strength. At 16,000 gauss, the value reached 6.3×10^{-4} volts. If the solution was neutral, the effect remained pretty well constant after excitation of the field.

Pure nickel from Kahlbaum in a 5 per cent solution of nickel sulfate gave an effect whose value could not be determined with certainty, but there was probably an effect one-fifth as large as that for iron.

A phenomenon regularly observed in solutions of both iron and nickel salts was an increase of the resistance of the solution the longer it was in the tube. For very small values of the E.M.F. the resistances were exceedingly high, up to 10^6 ohms, in the case of nickel solutions. For electromotive forces of a few volts, the resistance became only a few thousands of ohms.

All investigators who used pairs of electrodes made from the same material and dipped in a given solution, reported variable initial potentials no matter how carefully prepared the electrodes were.

Richards¹ prepared electrodes by reducing ferric oxide with hydrogen. The cells used consisted of a half cell containing reduced iron in an approximately normal ferrous

¹Richards, J. Am. Chem. Soc., 46, 89 (1924).

sulfate solution 0.01N in sulfuric acid and a normal calomel half cell connected by a salt bridge. A progressive decrease in the potential of the cell in the magnetic field from 0 to .001 volt during a period of 20 seconds was noted.

If, however, pure spongy reduced iron coated with electrolytic iron rich in occluded hydrogen was used, the original potentials of the cells were as much as 0.07 volt above the normal potentials and when the magnet was turned on, within 4 seconds a greatly accelerated fall of potential was always observed corresponding to an effect often twenty times as great as that produced in pure iron. The fall of potential was roughly proportional to the excess of potential shown by the occluded hydrogen.

Materials and Apparatus

The purpose of the present investigation was to study the effect of the magnetic field on the electrode potentials of iron and nickel under equilibrium conditions as nearly as possible. The metals used were from several different sources. The iron electrodes which gave the smallest and steadiest initial E.M.F.'s and the most reproducible results in the magnetic field were made either of soft Swedish iron sheet or ferrotype iron. The latter gave the better results of the two.

The electrodes were prepared as follows: Thin sheets of the metal were cut into narrow strips about 2-1/2 to 3 inches long. The surfaces were polished carefully with fine emery paper and covered with paraffin except for a small portion about 2 millimeters square. A paraffined cork stopper was split in the middle and the iron placed between the two halves of the cork. The stopper was then forced into the cell far enough to hold the electrode firmly in position and at the same time make the cell air tight.

The nickel electrodes were of two kinds: metal cut from a bar of pure nickel and electrolytic nickel plated on platinum wire.

The iron salt used was Baker's analyzed ferrous ammonium sulfate. An almost saturated solution of the salt was

acidified (about 0.003N) to prevent too great a change of ferrous ion concentration. Higher acid concentration permitted a troublesome evolution of hydrogen.

The distilled water used for the preparation of solutions was boiled to remove dissolved oxygen, then chilled quickly. The salt was finely powdered so that solution was rapid. The cell was then made up immediately and the stoppers sealed over with paraffin. In some cases, indicated in the table, the oxygen was removed more thoroughly: solutions were alternately outgassed with an oil pump and saturated with nitrogen under slight pressure. The cell was then swept out with nitrogen, filled with the solution, and sealed.

The nickel sulfate used was crystallized three times. The solutions were saturated with nickel hydroxide in order to make certain that the concentration of the salt would not change on account of precipitation of the hydroxide. The electrolytic nickel was plated from a solution of the composition used by Haring and Vanden Bosche.¹

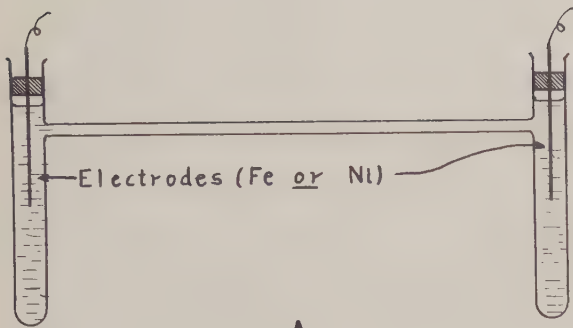
The type of cell first used (Figure 1, a) was made of two test tubes, 8-1/4 centimeters long and 1 centimeter in cross-section, flattened slightly for a greater part of the length to permit free circulation of oil about the tubes when they were placed in the narrow thermostat between the magnet poles. The test tubes which were to contain the electrodes

¹Haring and Vanden Bosche, Jour. of Phys. Chem., 33, 161 (1929).

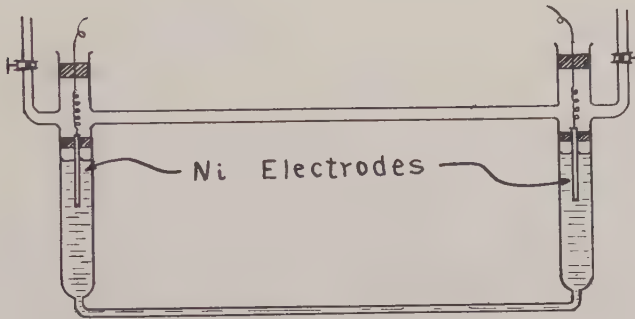
were then connected by a piece of 6 millimeter tubing. The total length of the cell was 17 centimeters. This length allowed one electrode to be in the center of the field while the other was sufficiently far removed that the effect of the field was negligible.

Because there was a tendency for the electrodes to be pulled up or down in the cork when the current in the magnet was turned on and thus allow air to leak into the cell, a slightly different type of cell (Figure 1, b) was used: Two test tubes were connected at the bottom by a piece of tubing. About 2 centimeters from the top of each electrode vessel was a similar connecting tube and directly opposite the opening of this cross piece on each test tube was sealed a side-arm closed by a stop-cock. The stopper holding the electrode was then forced into the cell past the first connecting tube after the cell had been filled with electrolyte and swept out with nitrogen. Each electrode had soldered to it a very fine copper wire coiled into a spring. The other end of the wire extended through another stopper in the top of each electrode vessel. After the stoppers were sealed in, the space above the lower and upper stoppers was swept out with nitrogen, then closed off by means of the stop-cocks. If the electrodes were moved slightly only nitrogen and not oxygen leaked into the cell.

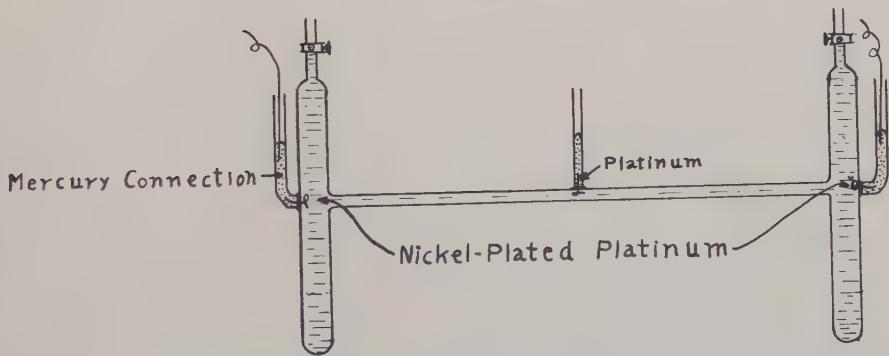
Still a third type of cell (Figure 1, c) was made when electrolytic nickel was used for the electrodes. Each of the



A



B



C

FIG. I.

two test tubes which were to serve as electrode vessels had sealed into it, just below the connecting tube, a platinum wire. The connecting tube also had a platinum wire sealed in at the middle. Each electrode vessel was closed at the top with a stop-cock. The electrolysis was first carried out in the cell with the two platinum wires in the electrode vessels as cathodes and the wire sealed in the connecting tube as the anode. The electroplating solution was then removed and the cell thoroughly cleansed with distilled water, alternately pumped out with the oil pump and flushed with nitrogen, then filled under nitrogen pressure. The solution had previously been pumped out and saturated with nitrogen.

The cell in use was placed in a small tank (12 mm. x 12 cm. x 32 cm.) made to fit between the poles of the magnet. By means of a small gear pump, oil was circulated through the tank from an oil thermostat so that the temperature did not vary more than $\pm 0.02^\circ$ at 20°C .

For the measurement of the E.M.F. of the cells, the potentiometric method was first used. Both potentiometer and galvanometer were at some distance from the magnet. The potentiometer was a Leeds and Northrup type K, No. 186625. The galvanometer was a Leeds and Northrup type R, with an internal resistance of 570 ohms.

Because it was possible that the potentiometer might be drawing so much current that it caused the E.M.F. of the cell to vary, a Dolezalek electrometer was used for some of

the measurements. The sensitivity of the electrometer is stated in the tables containing the data for experiments where it was used.

The magnetic field used in these experiments was produced by a powerful electromagnet constructed by Harkins and Kay.¹ The pole pieces were at a distance apart of 14 millimeters. The field strength at this distance, when a current of 36 amperes flowed through the magnet, was 13,000 gauss, measured by a fluxmeter and coil.

Experiments

As a review of the literature showed, no more than two, A. H. Bucherer and G. T. Elias, of the many investigators studied the effect of the magnetic field on the potential of iron under equilibrium conditions. Of these two, only one, Elias, used a magnetic field of sufficient strength to show the effect under the conditions of the experiment.

Since equilibrium conditions were desired, only ferrous and nickelous salts were used in any of the experiments. In the case of the iron salts, it was found by calculation that equilibrium conditions are unattainable. Either the hydrogen ion concentration is sufficiently great that hydrogen is replaced by iron or so low that ferrous hydroxide precipitates out.

¹Dissertation (University of Chicago), by W. B. Kay, 1928.

Neither iron nor nickel has ever given satisfactory reproducible electrode potentials. The state of division, method of preparation, mechanical strains, occluded gases, and the presence of certain gases in solution in the electrolyte, may all affect the potentials of these metals, and the present investigation reveals these or similar factors also influence the effect of the magnetic field on these metals.

An attempt was made to find a suitable electrolyte which would furnish ferrous ions. Potassium ferrocyanide containing potassium cyanide was tried but did not give a satisfactory equilibrium potential. The complex oxalate was also tried but it was unsatisfactory since hydrogen bubbles collected on the electrodes at least as rapidly as when ferrous sulfate was used. Ferrous ammonium sulfate was found to be the most suitable electrolyte. In some cases the solution was made about 0.003N in acid. This concentration of acid decreased the speed of the change in concentration of the solution by loss of ferrous ions, yet hydrogen was set free at a sufficiently slow rate that measurements could be taken if the bubbles were removed from the electrodes before a series of readings was taken. None of the cells had a constant potential. The best that could be done was to use a cell whose potential was changing so slowly that the superimposed effect of the magnetic field could be detected.

Although in every trial made, the two electrodes were cut from the same piece of metal and received similar treat-

ment, when they were put into the solution of the salt an initial E.M.F. varying from several ten thousandths to several tenths of a volt was noted. In order to steady the potential difference between the two electrodes, the greater part of the surface of each electrode was covered with paraffin. In some cases the electrode was covered completely and a very small drill used to expose the metal surface. This method was quite satisfactory when the electrometer was in use but increased the internal resistance of the cell to such a great extent that it could not be used at all with the potentiometer.

It was found that after standing several days, a cell which had been giving a decided change in E.M.F. in the magnetic field showed a decreased change and finally ceased entirely to give the effect. It was noted that in such cases the exposed portion of the electrode had turned black. If the electrode was removed from the cell, its surface scraped clean, and the electrode replaced in the cell, the original change in E.M.F. with the magnetic field was obtained. The coating was probably an oxide of the metal, since it was never formed on the electrodes in the cells which had been most carefully prepared.

When cells were used which gave an initial small and reasonably steady potential, the effect of the magnetic field on the E.M.F. of the cell was always of the sign predicted by theory, that is, if the positive electrode was exposed to the field due to its increased positiveness, the E.M.F. of the

cell increased. If the negative electrode was the one exposed to the field, the E.M.F. of the cell decreased. In no case did an effect in one direction appear and then reverse its direction unless the E.M.F. of the cell itself when not under the influence of the field had a tendency to change in this reverse direction. However, in cases where an equilibrium value had very apparently not been attained, such a phenomenon did occur at times.

As the tables of data and graphs show, the sign of the E.M.F. of the cell was not influenced by the direction of the current flowing in the magnet. The data and graphs of two typical cells are shown. The E.M.F. of Cell No. 1, Table No. II, was followed with the potentiometer. The electrometer was used for measurements in Cell No. 2, Table No. III. It is to be noted that there was always an immediate change in E.M.F., which was usually followed by a further slow change with time. The first change was so rapid that it was difficult to follow with the potentiometer, so that a lapse of time between the instant the switch was thrown and the first reading taken indicates that time was lost in obtaining the reading, not that the effect of the field was not immediate. The electrometer had such a long period that an elapse of a minute had to be allowed for the change of potential to be noted on the scale.

With iron, an increase of the current flowing in the magnet seemed not to effect any further change in E.M.F. of the cell after the current had reached 36 amperes.

A cell of two copper electrodes dipped in copper sulfate was tested to ascertain whether the magnetic field had an effect on the potential of non-magnetic metals in solutions of their salts. The result was negative.

Because of the difficulties involved in the preservation of a ferrous salt solution in contact with iron, it was decided to confine further investigations to the magnetic behavior of nickel in solutions of nickel sulfate.

As has been mentioned, the electrolyte was so prepared that there was no tendency for the metal to dissolve. Thus the possibility of the evolution of hydrogen was excluded and there was no precipitation of the hydroxide. However, both oxygen and hydrogen apparently greatly affect the potential of the nickel electrode.¹ Hence the precautions mentioned above were taken to outgas both the solutions and cells and exclude the entrance of air. As with iron, in cases where it was apparent that air had leaked into the cell, the exposed portion of the electrode turned black and masked the effect of the magnetic field.

Haring and Vanden Bosche noted the effect of hydrogen on the potential of nickel electrodes. Richards found that not only the original potential of iron was increased but the effect of the magnetic field on the potential was greatly affected by the presence of occluded hydrogen. Smith² remarked

¹Haring and Vanden Bosche, Jour. of Phys. Chem., 33, 1929.

²Smith, Jour. of Phys. Chem., 23, 186-202 (1919).

that there seemed to be a definite connection between the magnetic susceptibility of metals and their ability to occlude hydrogen.

Electrodes were coated with platinum black, rich in occluded hydrogen, and used as electrodes in solutions of dilute hydrochloric acid, ferrous ammonium sulfate, and nickel sulfate. This was done to make certain that platinum itself gave no effect in the magnetic field. There was no noticeable effect, either initially or after a period of time, when one electrode was placed in the magnetic field.

To test whether the initial difference in potential of two similarly prepared electrodes could finally be dissipated, the electrodes of the cell were shorted across various resistances. It was desirable to use a resistance approximately equal to the resistance of the cell. The calculated resistance of the electrolyte in the cell was about 6000 ohms but the measured resistance of the whole cell was between 25,000 and 30,000 ohms. After the electrodes had been shorted across 5000 ohms for 24 hours, the internal resistance had reached such a large value that the deflection of the galvanometer for a given excess potential supplied by the potentiometer was one-tenth its original value. This indicated that instead of dissipating the variable E.M.F. of the cell by this method, we had enormously increased its apparent internal resistance due to an increase in contact polarization.

The tables of data and graphs indicate that the ef-

fects obtained with nickel were similar to those obtained with iron; the effects are much greater than theory demands.

To test whether the values of the change of E.M.F. calculated from the equation given by Elias were of the correct order of magnitude, the following experiment was carried out with both iron and nickel. The object of the experiment was to determine the mechanical work in joules per mol done on the metal when it was drawn into the magnetic field and, from the value thus obtained, to calculate the E.M.F. to be expected.

Since hysteresis was small in the metals used for the electrodes, the process may be considered reversible for our purposes and the work may be considered equivalent to the change in free energy of the system on bringing it into the magnetic field from a point beyond the sphere of influence of the magnetic field. The following relationship exists between the work done on the metal and the E.M.F. of a cell consisting of one magnetized and one unmagnetized electrode in a solution containing ions of the metal,

$$-w = \Delta F = -E.N.F,$$

where $-w$ is the reversible work in joules per mol done on the cell, ΔF the increase in free energy of the system, or the decrease in free energy of the cell when it operates to give a current, E the E.M.F. of the cell, N the number of electrochemical equivalents of the metal per mol, and F the number of coulombs per equivalent.

The force exerted by the magnetic field on a weighed piece of metal at a given distance from the field was measured by means of calibrated phosphor bronze springs. The force was then calculated in dynes per mol for each metal and plotted against the distance from the center of the field. (Data, Table I; Graph, Figure 2) The area under the curve from the center of the field to the distance at which the force is greatest may then be set equal to the change in free energy per mol of the metal when it is drawn into the field.

The value of ΔF for iron read from the curve is 25.1 joules.

$$\Delta F = ENF$$

$$E = \frac{25.1}{2 \times 96,500} = 1.3 \times 10^{-4} \text{ volts}$$

The value for ΔF from the curve for nickel is 7.16 joules.

$$E = \frac{7.16}{2 \times 96,500} = 0.37 \times 10^{-4} \text{ volts}$$

Elias used the formula

$$E = \frac{B^2 \lambda}{8 \pi d}$$

to calculate the E.M.F. of magnetization and made the assumption, which he recognized as being at the best an approximation, that H , the field strength, was equal to B .

If, for purposes of comparison, we calculate the E.M.F. of the cell containing iron electrodes in the same way, we

TABLE I

Nickel		Iron	
Force (dynes/mol)	Distance (cm.)	Force (dynes/mol)	Distance (cm.)
59.3 x 10 ⁵	2.0	32.05 x 10 ⁵	0.6
88.95	2.5	33.33	0.6
210.5	3.3	69.05	1.1
151.2	3.9	97.72	1.5
88.95	5.4	182.41	1.8
69.97	5.4	602.6	2.1
53.68	6.4	801.3	2.6
30.26	7.3	667.7	3.0
23.87	8.6	534.2	3.6
18.6	9.7	364.82	4.3
18.4	19.7	254.07	5.0
10.7	11.0	214.98	5.6
5.7	12.4	218.89	6.3
4.4	13.6	141.37	7.2
3.2	15.6	93.81	8.2
3.2	16.2	59.06	9.4
1.9	17.5	33.35	10.6
5.18	15.3	24.23	11.7
4.05	16.3	13.81	13.2
2.39	16.9	7.95	14.3
1.34	16.9	4.36	16.0
0.77	18.5	3.71	18.1
0.26	20.0	0.6	19.5
0.16	21.4	0.4	20.9
0.096 x 10 ⁵	24.3	0.2	22.3
		0.95 x 10 ⁵	24.3

obtain

$$E = \frac{(13,000)^2 \times 55.84 \times 10^{-7}}{8 \times 3.1416 \times 7.8 \times 2 \times 96,500} = 2.6 \times 10^{-5} \text{ volts}$$

The value obtained from the experiment above is 1.3×10^{-4} volts, a value five times as great. This would indicate that the assumption made above is not valid and that perhaps the formula itself is not entirely correct.

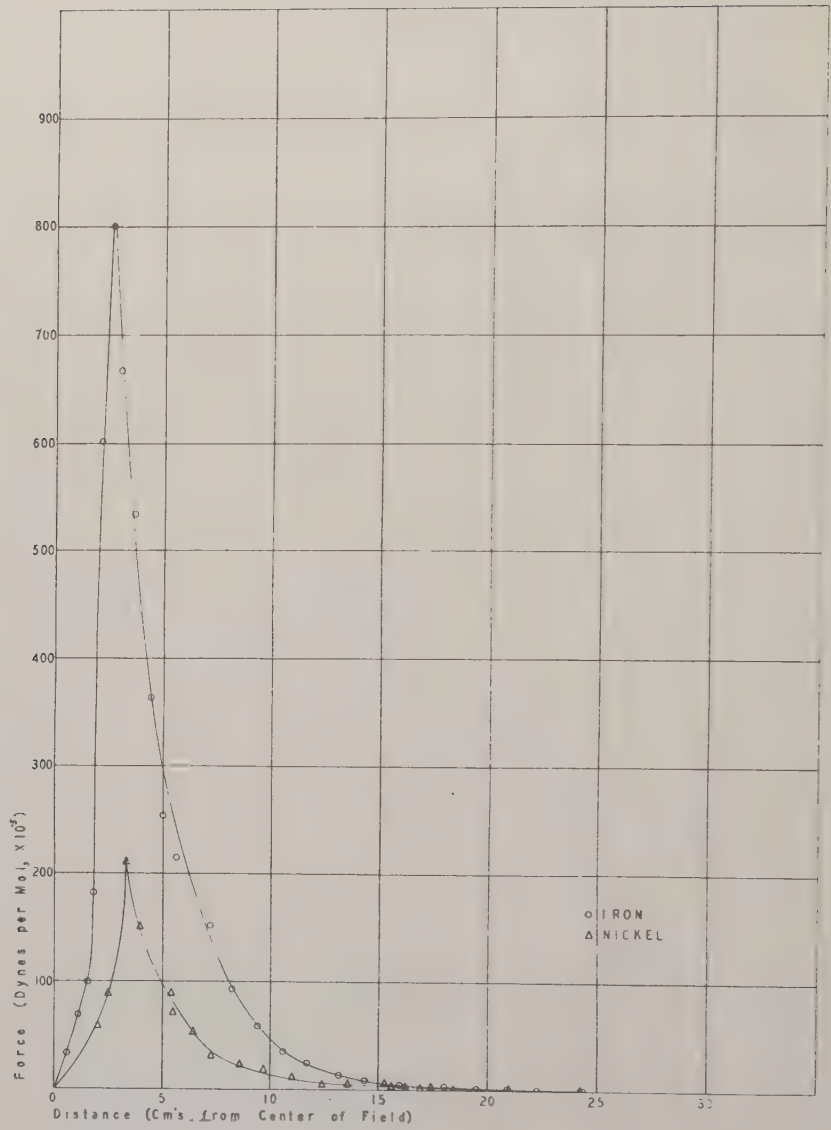


FIG 2

The behavior of Cell No. 2 may be taken as a typical example of the behavior of both iron and nickel cells in the magnetic field.

The graph is so plotted that the increasing positive character of the electrode in the magnetic field, be it originally positive or negative, is illustrated rather than an increase or decrease in the E.M.F. of the cell. It is to be noted that if the current is turned on in the magnet when the negative electrode of the cell is between the magnet poles, there is an immediate decrease in E.M.F. of the cell corresponding to an increase in the positive character of the electrode. If the positive electrode is in the field, the E.M.F. of the cell increases along with the increase in positive character of the metal.

After the initial change there may be a further slow change in the E.M.F. with time. In cases where the effect appears to become smaller while the metal is still under the influence of the magnetic field, the decrease may be attributed to the fact that the E.M.F. of the cell when not influenced by the magnetic field is changing in this same direction.

An increase in the current flowing in the magnet above 36 amperes increases the effect very little.

When the current in the magnet is turned off, the potential of the electrode between the poles decreases. The initial decrease is not so great as the initial increase,

probably because the metal does not lose its magnetization immediately.

In this cell the largest change in potential caused by magnetization was 0.003 volts, the smallest 0.0015 volts. This value is over twenty times the value which should be obtained according to the experimental calculation from the work done on the iron when it is drawn into the field and one hundred times larger than the value calculated from the formula of Elias. With some cells the actual change in E.M.F. was of the order of 0.01 volts.

The graphs for nickel (Figures 5 and 6) show that the nature of the effect is similar but the changes in E.M.F. sometimes amounted to as much or more than the changes for iron, whereas they should have been less than one-fourth as great.

The behavior of both iron and nickel electrodes in solutions of their salts indicated that equilibrium conditions had not been attained. The theoretical effect of the magnetic field on the potentials of these metals can not be expected to be obtained experimentally except under reversible conditions so that until the source of the excess effect is discovered and overcome further investigation of this phenomenon is at a standstill.

It would be interesting to find whether electrodes outgassed by a high frequency vacuum tube bombarder would still give this excess effect in the magnetic field. For

although we used all ordinary precautions against the presence of gases, there may still be enough gas remaining in the electrodes to affect greatly the electrode potential and the change of the potential in the magnetic field.

It might prove instructive to study temperature variations in the electrodes by means of a small thermocouple. A correlation between electromotive force changes and temperature variations might contribute to an explanation of the observed phenomena.

TABLE II
CHANGE IN E.M.F. IN MAGNETIC FIELD

Cell No. 1*
 $\text{Fe}, \text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2, \text{Fe}$

Time (minutes)	E.M.F. (volts)	Current in magnet (on or off)	Change in E.M.F. (volts)
<u>Positive Electrode between the Magnet Poles</u>			
0	0.00225		
2	0.00227		
4	0.002310		
7	0.002241		
9	0.002243		
11	0.002302		
12	0.002207		
13	0.002162		
13-1/2	0.002152		
15	0.006913	on	0.004761
15-1/2	0.007842		
16	0.008293		
17	0.008648		
18	0.008903		
19-1/2	0.009445		
21	0.009777		

(continued)

TABLE II (CONTINUED)

Time (minutes)	E.M.F. (volts)	Current in magnet (on or off)	Change in E.M.F. (volts)
<u>Positive Electrode between the Magnet Poles</u>			
24	0.009785		
27	0.009932		
28	0.007602	off	
30	0.005876		-0.002330
31	0.005107		
32-1/2	0.005578		
34	0.005820		
36	0.005913		
39-1/2	0.005298		
40	0.005052		
43	0.004523		
<u>Negative Electrode between the Magnet Poles</u>			
0	0.004054	off	
2	0.004463		
4	0.004355		
6	0.004327		
8	0.004394		
10	0.004295		
11	0.004255		
12	0.004207		
13	0.004183		
14	0.004175		
15	0.004172		
17	-0.008163	on	
18	-0.008953		-0.012335
19	-0.008075		
20	-0.008845		
21	-0.008540		
22	-0.008233		
24	-0.007986		
25	-0.007698		
27	-0.007425		
29	-0.006940		
30	-0.006680		
32	-0.006367		
33	-0.006077		
34	-0.005955		
36	-0.005417		
37	-0.005366		

(continued)

TABLE II (CONTINUED)

Time (minutes)	E.M.F. (volts)	Current in magnet (on or off)	Change in E.M.F. (volts)
<u>Negative Electrode between the Magnet Poles</u>			
39	-0.004790		
41	-0.004416		
43	-0.004487		
44	-0.004405		
47	-0.004115		
48	-0.003837		
		off	
50	-0.002162		-0.001675
53	-0.000503		
54	0.001480		
56	0.001702		
57	0.001910		
58	0.001915		
60	0.001935		

* The electrodes used were cut from a sheet of Swedish iron.
The potentiometer was used for measurements of E.M.F.

TABLE III

CHANGE IN E.M.F. IN MAGNETIC FIELD

Cell No. 2*
 Fe, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, Fe
 (in an atmosphere of nitrogen)

Time (minutes)	E.M.F. (volts)	Current in magnet	Change in E.M.F. (volts)
<u>Negative Electrode between the Magnet Poles</u>			
0	0.0049	0 amps	
13	0.0049		
20	0.0049		
22	0.0035	36 amps	-0.0014
23	0.0028		
24	0.0026		
25	0.0026		
26	0.0028		
27	0.0028		
28	0.0028	75 amps	0.0
29	0.0036		
30	0.0032		
31	0.0035		
32	0.0035		
33	0.0035	36 amps	0.0
34	0.0040		
35	0.0042		
36	0.0042		
37	0.0042		
38	0.0043	0 amps	+0.0001
39	0.0046		
40	0.0049		
41	0.0049		
56	0.0063		
		On - 36 amps Reverse direc- tion	
58	0.0049		-0.0014
60	0.0049		
61	0.0049		

(continued)

TABLE III (CONTINUED)

Time (minutes)	E.M.F. (volts)	Current in magnet	Change in E.M.F. (volts)
<u>Negative Electrode between the Magnet Poles</u>			
62	0.0049	75 amps	0.0
63	0.0046		
64	0.0044		
65	0.0044		
66	0.0042		
67	0.0042		
68	0.0042		
69	0.0042		
70	0.0042	36 amps	0.0
71	0.0042		
72	0.0042		
73	0.0042		
74	0.0042		
75	0.0042		
76	0.0047	0 amps	+0.0005
77	0.0047		
78	0.0047		
79	0.0049		
80	0.0049		
81	0.0050		
82	0.0050		
<u>Gas Bubbles Shaken Loose from Electrodes and Positive Electrode Placed between Magnet Poles</u>			
0	0.0021	36 amps	+0.0021
1	0.0026		
2	0.0025		
3	0.0021		
4	0.0021		
5	0.0042		
6	0.0042		
7	0.0042		
8	0.0037		
9	0.0035		
10	0.0032		

(continued)

TABLE III (CONTINUED)

Time (minutes)	E.M.F. (volts)	Current in magnet	Change in E.M.F. (volts)
<u>Gas Bubbles Shaken Loose from Electrodes and Positive</u> <u>Electrode Placed between Magnet Poles</u>			
10-1/2	0.0028	75 amps	-0.004
11	0.0028		
12	0.0030		
14	0.0032		
15	0.0033		
16	0.0032	0	+0.0021
17	0.0016		
18	0.0014		
19	0.0014		
20	0.0014		
21	0.0014		
39	0.0021		
40	0.0042	75 amps Reverse direction	
41	0.0042		
42	0.0049		
43	0.0049		
44	0.0049		
45	0.0049		
46	0.0049		
46-1/2	0.0035	0	-0.0014
47	0.0028		
48	0.0025		
49	0.0021		
50	0.0021		

*Electrodes were of ferrotype iron. The hydrogen ion concentration was about 0.003N. Readings were made with the electrometer. A deflection of 1.4 millimeters corresponds to one millivolt.

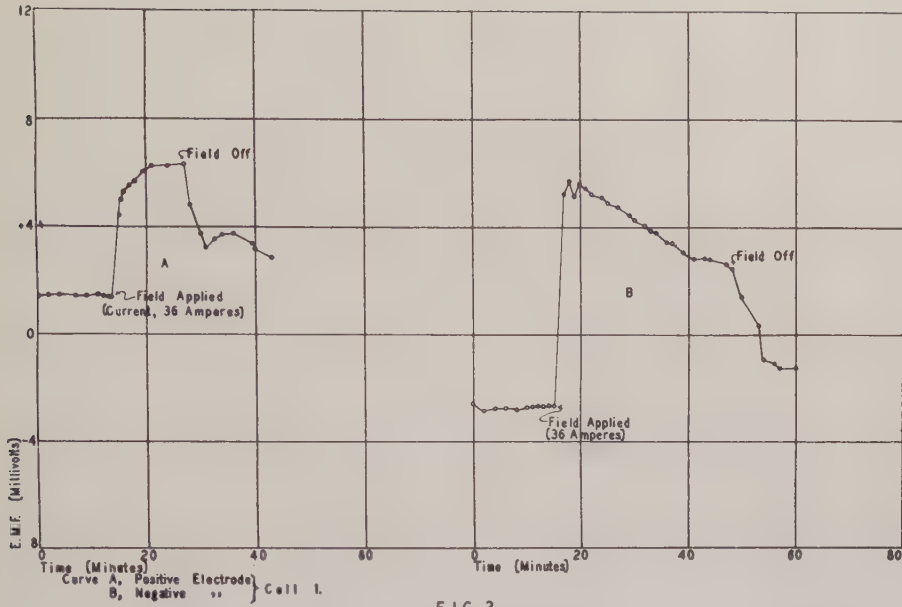


FIG. 3.

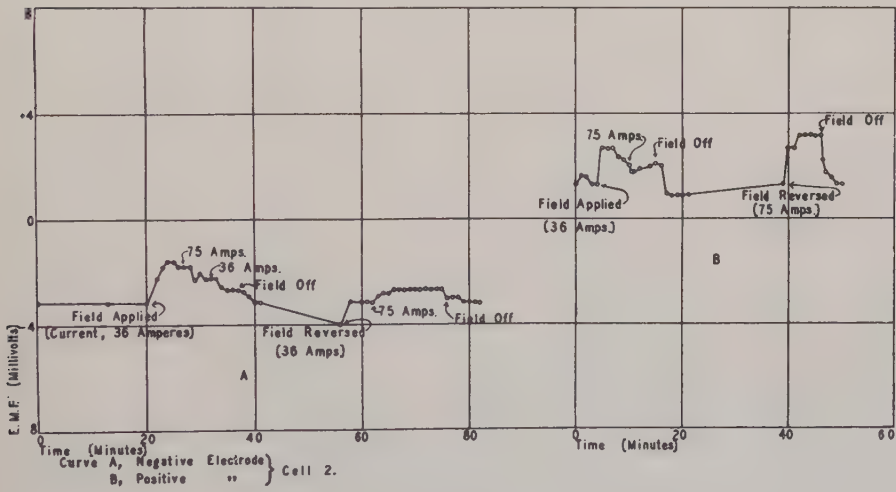


FIG. 4.

TABLE IV
CHANGE IN E.M.F. IN MAGNETIC FIELD

Cell No. 3*
Ni, $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2$, Ni
(in an atmosphere of nitrogen)

Time (minutes)	E.M.F. (volts)	Current in magnet	Change in E.M.F. (volts)
<u>Negative Electrode between the Magnet Poles</u>			
0	0.0585		
6	0.0581		
7	0.0581	36 amps	0.0
9	0.0560	75 amps	-0.0021
10	0.0557		
12	0.0581	0	+0.0024
13	0.0609		
14	0.0616		
15	0.0602	75 amps Reverse direction	-0.0014
16	0.0567		
17	0.0560		
18	0.0562		
19	0.0562		
20	0.0564		
21	0.0560		
22	0.0567	0	+0.0003
23	0.0616		
24	0.0623		
25	0.0627		
26	0.0630		
27	0.0630		
28	0.0634		
29	0.0569	75 amps Original direction	-0.0065
30	0.0581		
31	0.0581		

(continued)

TABLE IV (CONTINUED)

Time (minutes)	E.M.F. (volts)	Current in magnet	Change in E.M.F. (volts)		
<u>Negative Electrode between the Magnet Poles</u>					
32	0.0581	0	+0.0007		
33	0.0585				
34	0.0588				
35	0.0588				
36	0.0595				
38	0.0637				
40	0.0644				
42	0.0644				
43	0.0644	75 amps	+0.0007		
48	0.0646				
<u>Positive Electrode between the Magnet Poles</u>					
0	0.0602				
2	0.0602				
4	0.0602				
5	0.0602				
7	0.0609				
9	0.0623				
10	0.0630				
10-1/4	0.0686				
11	0.0672				
12	0.0669				
13	0.0672				
14	0.0674				
15	0.0679				
15-1/2	0.0672	0	-0.0007		
16	0.0658				
17	0.0644				
18	0.0641				
19	0.0637				
20	0.0651				
20-1/4	0.0686				
21	0.0686				
<u>75 amps Reverse direction</u>					
20	0.0651	75 amps Reverse direction	-0.0006		
20-1/4	0.0686				
21	0.0686				

(continued)

TABLE IV (CONTINUED)

Time (minutes)	E.M.F. (volts)	Current in magnet	Change in E.M.F. (volts)
<u>Positive Electrode between the Magnet Poles</u>			
22	0.0679	0	+0.0021
23	0.0679		
24-1/2	0.0679		
25	0.0658		
26	0.0641		
27	0.0630	75 amps Original direction	+0.0007
28	0.0623		
29	0.0623		
29-1/2	0.0623		
30	0.0630		
31	0.0662		
32	0.0669		
33	0.0679		
34	0.0683		
35	0.0686		
36	0.0651	0	-0.0035
37	0.0623		
38	0.0609		
39	0.0596		
40	0.0588		
41	0.0581		
42	0.0574		
43	0.0574		

*The electrometer was used for measurements of E.M.F. One millimeter deflection corresponded to 1.4 millivolts.

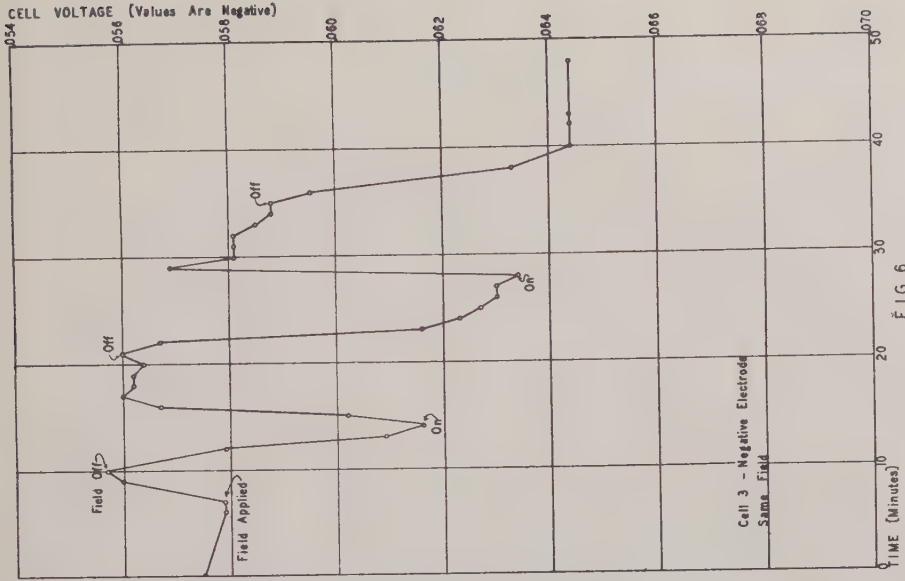


FIG. 6.

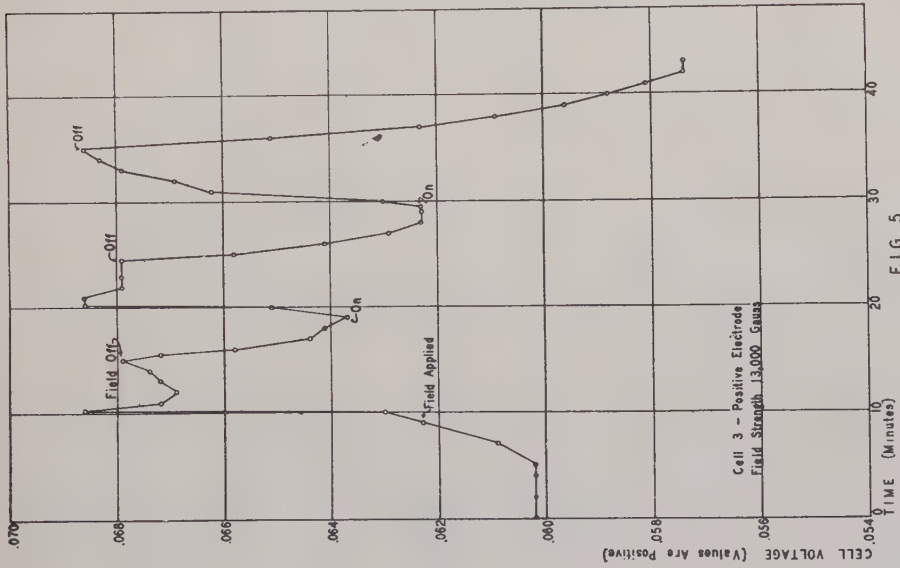


FIG. 5.

SUMMARY

By measurements of the E.M.F. of the cell,

Fe (magnetized), $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, Fe (unmagnetized)

it has been found that the effect of magnetization on the electrode potential of iron is to increase its electro-positive character in accord with the theory of Elias. Numerical data have been obtained and graphs made to show that the effect of a magnetic field on the electrode potential of nickel is similar to the effect on iron.

The magnitude of the actual effect for both iron and nickel was found to exceed that required by theory, an indication that equilibrium conditions had not been obtained.

It was found that the potential difference between two similar electrodes of nickel could not be dissipated by short-circuiting the electrodes through a resistance. The effect of the short circuit was to increase the contact polarization.

An experiment was performed to determine the E.M.F. to be expected on magnetization of one electrode for the cells,

Fe (magnetized), $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, Fe (unmagnetized)

and

Ni (magnetized), NiSO_4 , Ni (unmagnetized)

The values obtained were, respectively, 1.3×10^{-4} volts and 0.37×10^{-4} volts.

It was found that the potentials of the following cells were not affected by the magnetic field:

Cu, CuSO_4 , Cu

Pt + H_2 , HCl (dil.), Pt + H_2

Pt + H_2 , $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, Pt + H_2

Pt + H_2 , NiSO_4 , Pt + H_2

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